Vibrational Spectra of Nitrogen in Simple Mixtures at High Pressures¹

M.E.Kooi^{2,4}, L.Ulivi³, and J.A.Schouten²

¹ Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

² Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65, 1018
XE Amsterdam, The Netherlands

³ Istituto di Elettronica Quantistica, CNR, Via Panciatichi 56/30, 50125 Firenze, Italy

⁴ To whom correspondence should be addressed.

ABSTRACT

Previous investigations have revealed a considerable difference between the

spectral behavior of a molecule in a pure substance and in a mixture. To get more in-

sight in the influence of the intermolecular interaction and of the mass of the molecules

we have performed high resolution measurements of the linewidths and peak positions

of the vibrational Raman spectrum of pure nitrogen, nitrogen in argon and nitrogen in

helium. The research has been carried out at room temperature and at pressures up to the

melting line. It turns out that, in contrast with expectation, the linewidth as well as the

frequency shift are essentially the same for pure nitrogen as for nitrogen diluted in ar-

gon, although both the mass and the potential well depth are quite different. The ex-

perimental results show the same tendency as recent computer simulations.

KEY WORDS: dilute mixtures; high pressure; high resolution raman spectroscopy; line

width; nitrogen.

1. INTRODUCTION

The characteristic behavior of the vibrational frequency of (diatomic) molecules in the fluid phase as a function of pressure - a red shift at low pressures followed by a blue shift at higher pressures - has been the subject of many experimental and theoretical studies [1,5]. The shift of the frequency with respect to that of an isolated molecule reflects the effect of the average intermolecular forces exerted by the surrounding medium. An important aspect is the change in these forces due to the change in bondlength at excitation [6]. Much less attention has been paid to the profile of the spectrum [7]. In a pure component the intermolecular forces establish, in combination with the momentary density distribution, also the momentary frequency distribution, whose spread is called the amplitude of modulation. The shape of the *measured* spectrum and its linewidth, however, are affected by the dynamics of the system. In a mixture, also concentration fluctuations play a role [8], in addition to density fluctuations, and the dynamics may be essentially different.

In a previous experimental study on the binary system helium-nitrogen it has been shown [3] that in a dilute solution of nitrogen the shift is much larger than in pure nitrogen and that the red shift does not occur. The linewidth has also been reported for nitrogen and nitrogen in helium but due to the experimental resolution the accuracy was limited. Nevertheless, it was clear that the linewidth was smaller in the mixture than in the pure substance.

Calculations using hard fluid theory [9] and computer simulations show that in diluted solutions of nitrogen in helium the (positive) bond-length independent contribution of the molecular interaction to the shift is smaller than the experimental value, in contrast with the situation in pure systems. The tendency of the linewidth as a function

of pressure, obtained from computer simulations, is the same as in the experiment but the absolute value of the width could not be compared due to the experimental uncertainty. An interesting result is that in the dilute mixture the linewidth is related primarily to the properties of the diluent and to a much lesser extent to the interactions between nitrogen and helium molecules. Recently, simulations have been performed for nitrogen diluted in argon [10] and the results have been compared with those of the previous systems. To make the comparison complete, we have carried out a high resolution Raman study of the frequency and linewidth of pure nitrogen and of nitrogen in argon. A useful comparison is only possible if the resolution is higher than in previous measurements. Moreover, some preliminary measurements have been carried out for dilute mixtures of nitrogen in helium.

2. EXPERIMENTAL METHOD

All measurements have been performed at room temperature. The pressure was generated in a diamond anvil cell (DAC) of the membrane type. For the pressure measurement the ruby method was used with the scale of Mao et al. [11]. R1 lines of the ruby spectra were measured using a portable spectrometer, which was calibrated using a neon lamp before each measurement. To improve the accuracy of the pressure measurements the reference wavelength R1 at ambient pressure was measured for each individual ruby chip. The mixtures were prepared in a gas filling system. A mixing time of at least 24 hours was taken to allow for proper mixing.

An argon-ion laser with an intracavity etalon was used in single mode operation. We made sure that the power of the laser was low enough during the pressure measurement to prevent heating of the ruby chip. The reference wavelength R1 at ambient pres-

sure was measured with a laser power of 2.5 mW. For the Raman measurements the power of the laser was increased till 300 mW.

A polarisation rotator has been used to obtain the maximum grating efficiency. The laser was focused into the sample by a microscope objective and after the DAC a second microscope objective has been placed. The signal was dispersed by a double monochromator and detected by a photomultiplier tube. The double-pass double monochromator spectrometer (DMDP 2000) described by Mazzacurati et al. [12] was used in the single pass configuration to increase the efficiency of the instrument. All signals were measured with an entrance slit width of 100 µm. This leads to an instrumental profile (almost Gaussian) with a width (FWHM) of about 0.15 cm⁻¹.

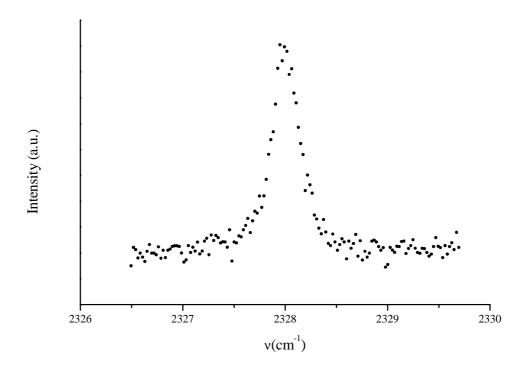


Fig. 1. Typical Raman spectrum of N_2 in N_2 -Ar, x[Ar]=0.06, at 0.6 GPa and 299 K.

Before and after each Raman measurement the spectrograph was calibrated using the neon lines of 549 nm and 553 nm respectively. This gives an accuracy of about 0.1 cm⁻¹ in the absolute wavenumber.

The Raman spectra have been fitted with Lorentzian curves as for most of the spectra a Lorentzian resulted in a better fit than a Gaussian according to the least squares approximation method. These fits have been used to determine the peak position and the FWHM. The instrumental FWHM of 0.15 cm⁻¹ is subtracted quadratically from the measured width. A typical Raman spectrum is presented in Figure 1.

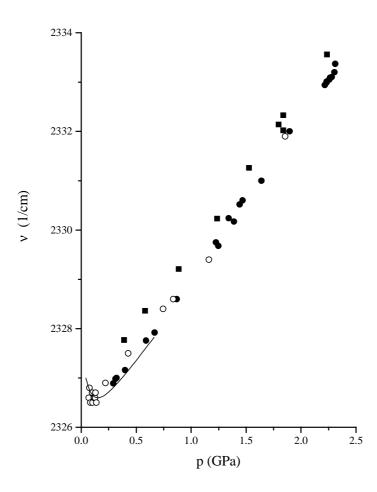


Fig. 2. Raman frequency of pure nitrogen at room temperature as a function of pressure. Squares, this work; open dots, ref. 1; solid line, ref. 2; full dots, ref. 3.

DISCUSSION

With respect to the vibrational frequency of pure nitrogen the pressure dependence is in good agreement with previous experimental data [1-3] as shown in Figure 2, but there is a slight systematic deviation towards higher values of about 0.5 cm⁻¹ corresponding to about 0.15 GPa. We can not explain this difference considering the experimental procedure for the frequency as well as the pressure measurements. However, since we are interested in the *difference* between the pure substance and the dilute mixture the deviation is not relevant for the further discussion. In the high density fluid the

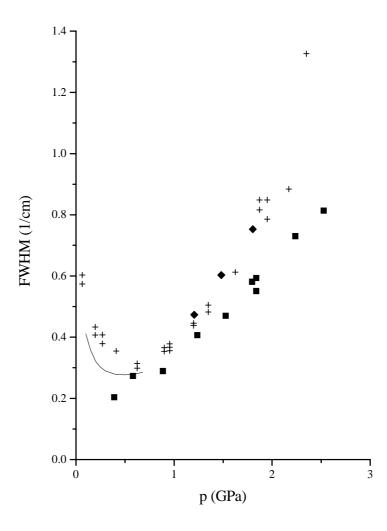


Fig. 3. FWHM of the Raman peak of pure nitrogen at room temperature as a function of pressure. Squares, this work; solid line, ref. 21; diamonds, ref. 8; crosses, ref. 13-15.

frequency is an almost linear function of pressure from 0.5 to 2.5 GPa.

The linewidth is plotted in Figure 3. The scatter in the data is small. In general the results of this work are in good agreement with those of earlier investigations [2,3,13-15]. Our data set forms a good continuation of the accurate work of Lavorel et al. [2]. The values are slightly lower than those of Ref.3 and of Refs.13-15. The experimental data obtained from T_2 measurements [13-15] show a tendency for a sharper increase near the melting line. In this study we have extended the measurements just into the metastable fluid region to investigate this effect. Our results do not show this tendency but it turns out that above 1 GPa the linewidth is almost a linear function of pressure. A comparison with the values obtained from computer simulations [5] reveal, as before, that the results agree quite well. Simulations performed without the dispersion correction give a slightly lower value for the linewidth.

The vibrational frequency of nitrogen in the argon-nitrogen mixtures (5.9 mole% nitrogen) is shown in Figure 4. The value of the frequency is lower than in pure nitrogen (solid line) but the difference is less than 1 cm⁻¹. In the case of nitrogen in helium the frequency was much higher in the mixture than in the pure substance. As mentioned in the introduction, the red shift of the frequency is attributed to the change in bondlength at excitation of the nitrogen molecule and the resulting change in intermolecular interaction. Another way of saying is that the solvation energy for an excited molecule is different from that of a non-excited molecule. In the case of pure nitrogen this change is negative. Since the potential depth of helium is very small the effect is also small and the red shift is absent. The potential well of argon is 25% deeper than that of nitrogen and, therefore, the observed shift, negative with respect to the pure component, is in agreement with the expected behavior. Figure 4 also shows the results of computer

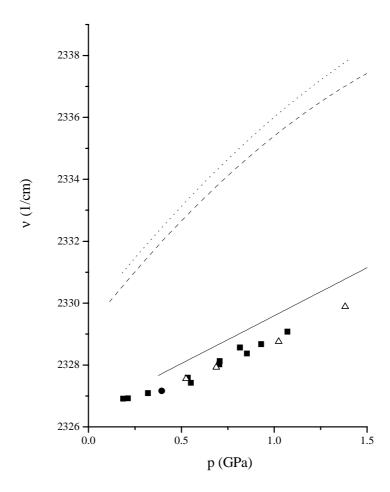


Fig. 4. Raman frequency of N_2 diluted in Ar and pure N_2 as a function of pressure. This work: squares, 5.9 mole% N_2 ; triangles, 3.0 mole% N_2 ; dot, 2.9 mole% N_2 ; solid line, pure N_2 .; Computer simulations: dashed line, pure N_2 [ref. 5]; dotted line, N_2 diluted in Ar (0 mole%) [ref. 10].

simulations. The frequency, calculated with the bond length independent potential, is slightly higher for nitrogen in argon than for pure nitrogen. The dispersion correction is about 20% larger than for the mixture than for the pure substance.

Measurements have also been performed for a mixture with 3% nitrogen. The results coincide with those of 6% nitrogen as far as the frequency is concerned. This could be expected since there is hardly any difference between the frequency of pure

nitrogen and that of a 6% mixture and since the frequency changes almost linearly as a function of the volume fraction [8].

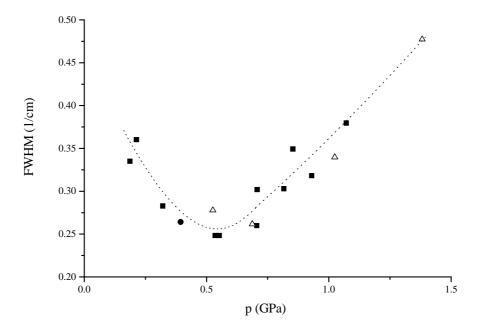


Fig. 5. FWHM of the Raman spectrum of N_2 diluted in Argon. Squares, 5.9 mole% N_2 ; triangles, 3.0 mole% N_2 ; dot, 2.9 mole% N_2 ; dotted line, guide to the eyes.

In Figure 5 the linewidth of nitrogen in argon is given for mixtures with 5.9 and 3.0 mole% nitrogen. The linewidth first decreases as a function of pressure and then increases via a minimum at about 0.6 GPa. The behavior is the same as for the pure substance. The minimum is at about the same pressure and the absolute value of the width at a certain pressure is also the same within the experimental accuracy. This is in contrast with the results of nitrogen in helium in which case the minimum shifts towards about 1GPa and the linewidth is much smaller than in the pure substance. A detailed analysis of the time correlations of the various contributions to the vibrational frequency in a dilute mixture, using computer simulations, revealed that the smaller linewidth is

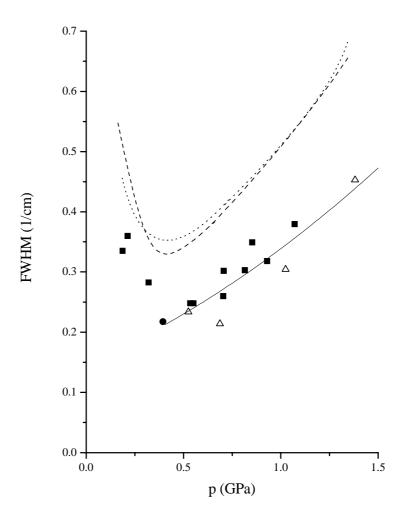


Fig. 6. Comparison between the measured and the calculated FWHM of the Raman spectrum of N_2 in pure N_2 and N_2 diluted in Ar. This work: squares, 5.9 mole% N2; triangles, 3.0 mole% N2; dot, 2.9 mole% N2; full line, pure N_2 . Computer simulations (with dispersion correction): dashed line, pure N_2 [ref.5]; dotted line, N_2 diluted in Ar (0 mole%) [ref. 10].

mainly due to the smaller mass of helium and the predominantly repulsive interaction between helium atoms [16]. The interaction between helium and nitrogen is almost irrelevant. Since the mass of the argon atom is almost 50% more than that of the nitrogen molecule and since the argon potential well depth is 25% deeper one would also expect

a difference in linewidth. The two effects might compensate each other or the rotational degrees of freedom play a role. Meanwhile, simulations have also been performed for argon-nitrogen [9]. The curves for an infinitely dilute mixture and for the pure substance are plotted in Figure 6. It is interesting to note that also the calculated curves nearly coincide. The calculated lines are broader than the experimental ones.

Actually, the comparison with pure nitrogen and with the simulations should only be made for the infinitely dilute mixture because critical broadening might play a role, as in the case of helium-nitrogen. Therefore, we have also carried out some measurements for a mixture with 3.0% nitrogen. The accuracy is not so high because the signal is very weak. The linewidth is the same within the experimental accuracy.

Preliminary measurements have been performed for helium-nitrogen. Literature values for the linewidth are not available for pressures below 2.5 GPa and the data are not very accurate. Data have been collected for mixtures with 4.0% and 3.2% nitrogen. Since the compositions are very close and considering the experimental uncertainty these data are not suitable for extrapolation at zero concentration. More measurements with a lower nitrogen concentration (2% or less) are in progress. However, if the available data are used to calculate the values for an infinitely diluted mixture the results indicate a lower value for the linewidth than assumed in Ref.17. This suggests that the quantitative agreement with the simulations is better.

ACKNOWLEDGMENTS

The experimental work as been performed at LENS, Laboratorio Europeo di Spettroscopie Non-Lineari, Firenze, Italy, under the European Community contract TMR-ERBFMGCT-950017.

REFERENCES

- 1. G.S.Devendorf and D.Ben-Amotz, *J.Phys.Chem.* **97**: 2307 (1993).
- 2. B.Lavorel, B.Oksengorn, D.Fabre, R.Saint-Loup, and H.Berger, *Mol.Phys.* 75: 397 (1992).
- 3. M.I.M.Scheerboom, J.P.J.Michels, and J.A.Schouten, *J.Chem.Phys.* 104: 9388 (1996).
- 4. M.Ridder, A.A.Suvernev, and T.Dreier, *J. Chem. phys.* **105**: 3376 (1996).
- 5. J.P.J.Michels, M.I.M.Scheerboom, and J.A.Schouten, *J.Chem.Phys.* 103: 8338 (1995).
- 6. L.E.S.de Souza, C.B.E.Guerin, D.Ben-Amotz, and I.Szeifler, *J.Chem.Phys.*99:
- 7. J.Chesnoy and M.Gale, *Adv. Chem. Phys.* **70:** 297 (1988).
- 8. M.I.M.Scheerboom and J.A.Schouten, *Phys.Rev.E* <u>51</u>: R2747 (1995).
- 9. K.S.Schweitzer and D.Chandler, *J. Chem. Phys.* **76:** 2296 (1982).
- 10. J.P.J.Michels, M.E.Kooi, and J.A.Schouten, to be published.
- 11. H.K. Mao, J. Xu and P.M. Bell, *J. Geophys. Res.* **91**: 4673 (1986).
- 12. V. Mazzacurati, B. Benassi and G. Ruocco, *J. Phys. E: Sci. Instrum.* 21: 798 (1988).
- 13. R. Kroon, R. Sprik and A. Lagendijk, *Chem. Phys. Lett.* **161**: 137 (1989).
- 14. R. Kroon, M. Baggen and A. Lagendijk, *J. Chem. Phys.* **91**: 74 (1989).
- 15. R. Kroon, thesis, University of Amsterdam, Amsterdam, (1993).
- 16. J.P.J.Michels and J.A.Schouten, *Mol.Phys.***90**: may (1997).
- 17. J.P.J.Michels, M.I.M.Scheerboom, and J.A.Schouten, *J.Chem.Phys.* 105: 9748 (1996).